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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]Especially this invention relates to the use as precipitated silica, for example, abrasive soap in a transparent toothpaste composition, about synthetic amorphous silica.

[0002]

[Description of the Prior Art]The toothpaste composition is fully characterized in literature and many constituents are indicated in a patent specification and other articles. A toothpaste composition contains many specific ingredients, for example, abrasive soap, the source of fluoride, a binding material, an antiseptic, a moisturizer, a dental plaque inhibitor, colorant, water, a flavor agent, and other alternative ingredients. In these ingredients, abrasive soap is required to give removal of moderate washing and a dental plaque, without exposing the gear tooth itself to wear superfluously. Typically, as for a toothpaste composition, about 5 thru/or 50 % of the weight of abbreviation contain the abrasive soap of ** to about 30 % of the weight preferably. The abrasive soap by which normal use is carried out is alumina, calcium carbonate, and calcium phosphate. Synthetic silica is more nearly recently used on account of the efficient detergency, compatibility with other ingredients, and a physical characteristic. The important characteristic of the silica used in a transparent toothpaste composition is an apparent refractive index, and the more this value is low in selected water / moisturizer system, the more it can use more water in that transparent toothpaste. For example, a thing like sorbitol for which a more expensive moisturizer is replaced with water becomes saving of remarkable cost.

[0003]This invention persons showed that it could adjust when the refractive index of the appearance of amorphous silica chooses the processing condition under manufacture of silica carefully. By changing these conditions, the basic feature of the overall fine-pores size

distribution which exists in amorphous silica is changed, and this ranks second and determines an apparent refractive index.

[0004]When are stated more to details and the grade of a super-micropore (less than 0.7 nm) that water can be adsorbed preferentially contacts silica to a moisturizer/drainage system, it is thought that main roles are played. A super-micropore as such small fine pores that it is enough to except nitrogen molecules. Classified [characterization OBU porous SORIZZU (Characterization of Porous Solids): The Anh introductory survey (Anh.) of characterization OBU porous SORIZZU II Introductory Survey -Kenneth S W Synge (Kenneth SW Sing), 1991, ERUSHIE beer science pub RISSHASU (Elsevier Science Publishers), and Amsterdam].

[0005]The example of the precipitated silica useful as abrasive soap of toothpaste which has the structure of a degree in the middle from low, British ***** No. 1482354 and ** No. 1482355 [Hoover (Huber)], It can find out to European patent application 0227334 and 0236070 [unilever Bar (unilever)], European patent application 0143848, and 0139754 [Taki (Taki)]. British ***** No. 1482354 and ** Although the silica for using it for No. 1482355 in common toothpaste is indicated, it is not indicated about use in transparent toothpaste. In the European patent application 0227334 and 0236070, the silica unsuitable for blending into transparent toothpaste is indicated.

[0006]In European patent application 0143848 and 0139754, the silica which has a refractive index of an usable texture and appearance in transparent toothpaste is indicated. these patents -- 1.455. or -- Refractive index (apparent refractive index) of the appearance of the range of 1.47 The manufacturing method of the amorphous silica which it has is indicated. This gives an amorphous phase in calcination at 1100 ** to the X-rays which have the BET surface area of the specific range.

European patent application 0143848 is indicating the BET surface area of 270 - 500m²/g, and is indicating the BET surface area of European patent application 0139754 5-60-m²/g.

[0007]

[Problem(s) to be Solved by the Invention]The amorphous precipitated silica of this invention provides the characteristic of the new range of combining high level polish nature and the good transparency in the refractive index of low appearance when blended with a toothbrushing constituent. The level of the polish nature obtained by the silica of this invention is unusually high, seeing from a point of the patency of the structure about [which is defined by measurement of the adsorptivity of an oil, and porosity] high which the silica has. Such polish nature in particular of the high level connected to the transparency of good toothbrushing in the refractive index of low appearance was not obtained depending on using precipitated silica conventionally.

[0008]

[Means for Solving the Problem]Even if silica of this invention is a comparatively low particle

size (namely, 5-10 microns), also when particle size distribution is minutely adjusted so that coarse particles and what is larger than especially 30 micrometers may be excepted, it can provide high level polish nature. It is admitted that polish nature of amorphous silica can be enlarged by extending particle size distribution so that particles of higher percentage may exceed 20 microns, but such a material may produce taste which cannot be permitted when blended into toothpaste.

[0009]Silica can be prepared by using a low-concentration cation, for example, calcium, and magnesium, washing a filter cake using deionized water, and showing outstanding stability, when dry output is blended with toothpaste which contains fluoride ion after that.

[0010]Generally, there is no meaning in characterization by high level patency and nitrogen absorption art of pore structure of silica containing larger fine pores not much. It is because such art is useful to fine pores of a diameter up to about 60 nm, i.e., micropore (micropore) (up to 2 nm) and the meso fine pores (meso-pore) (2-50 nm). In order to measure the porosity of a total range which exists in such a material, it is required to, use oil adsorption or an option like mercury porosimetry for example. Since output of this invention is carrying out the owner of pore structure over 60 nm, i.e., the macropore, (macropore) considerably, it needs to give a definition by such art.

[0011]A similarly important thing in amorphous silica is existence of a micropore (diameter below 2 nm) and a super-micropore (diameter below 0.7 nm) undetectable by nitrogen absorption measurement in particular. It is shown by shift of a refractive index of that appearance when amorphous silica contacts a moisturizer/drainage system the how much of a fine-pores size distribution fine pores of this range occupy. Density of amorphous silica to helium is assumed to give discernment to existence of a super-micropore, and since silica is further characterized by these measurement, it is used.

[0012]This invention is i abbreviation 100 thru/or 450-m²/g. BET surface area, ii) a weighted mean particle size (however, less than 10% of weight particle size distribution -- 20 microns -- size.) of 5 micron thru/or 15 microns And less than 5% of preferably from what is been size, and iii 16 [about] more preferably than 25 microns from about 20 to about 26, Preferably A plastic wear value (plastics abrasion value) of a range to about 24, iv) From 3 nm, preferably about 12 nm about 2 nm Average pore diameters up to 9 nm, v) amorphous silica which has the oil absorbcency of the range of 130cm³/transmissivity [of at least about 70%] and vi 70 thru/or 100g in the refractive-index range of 1.430 thru/or 1.433 -- provide precipitated silica preferably.

[0013]Silica of this invention had a crystal structure of alpha cristobalite after calcination at 1100 **.

[0014]these plastic wear values -- an average (mean) -- 117 (PAV 16) thru/or average 195 (PAV26). It is equivalent to a radioactive dentine wear (RadioactiveDentineAbrasion) (RDA)

value of average 179 (PAV 24) and average 148 (PAV 20). These were obtained from correlation in which it has a correlation coefficient (99% of reliability) of 0.91 between PAV and RDA about silica of 15 which has PAV of the range of 7.5 thru/or 31.

[0015]Usually, moisture content of silica is less than about 25%/w/w, and it is preferred that it is less than about 15%/w/w.

[0016]As for a transparent toothpaste composition of this invention, about 5 thru/or 50 % of the weight of abbreviation contain amorphousness of this invention up to about 30 % of the weight, and precipitated silica preferably.

[0017]They of silica of normal routine this invention are physical, and it is defined by chemical property. The standard test method used to these characteristics is as follows.

[0018]Surface area : Surface area i) Brunauer (Brunauer), Emmet (Emmett), And soap tea (Sorpty) 1750 which used the teller's (Teller) standard nitrogen absorption method (BET adsorption method), and was supplied from the Carlo Erba company (Carlo Erba company) of Italy It determines using the single pointing method by a device. A sample is under a vacuum before measurement. Degasifying was carried out at 270 °C for 1 hour.

[0019]ii) oil absorption : opt for oil adsorption by the ASTM spatula kneading [together] method (spatula rubout method) (American Society of Test Material, standard D, 281).

[0020]This examination is based on a principle of mixing of linseed oil by kneading together until a paste of the shape of hard putty which is not divided or separated forms, when it cuts with a spatula on the smooth surface using a spatula, and silica : which puts volume of a used oil into the following formulas -- oil absorption $= (\text{oil absorption cm}^3 \times 100) / (\text{weight g of silica sample}) = \text{cm}^3 \text{ oil} / 100 \text{ g silica}$.

[0021]iii) Weighted mean particle size : measure a weighted mean particle size of silica by Malvern Master sizer (Malvern Mastersizer) using a lens of course length of 45 nm. This device manufactured by the Malvern INSU torr face (Malvern Instruments) of WOCE Tasha (Worcestershire) and Malvern (Malvern), Low-power output helium/Ne laser is used and a principle of the Fraunhofer diffraction is used. Before measurement, a sample was underwater distributed for 7 minutes using an ultrasonic wave, and aqueous suspension was formed. The Malvern Master sizer measures weight particle size distribution of silica. A number (d_{90}) is easily obtained from data obtained by this device for a number (percentile) (d_{10}) and about 9000 minutes for a weighted mean particle size (d_{50}) and about 1000 minutes.

[0022]iv) plastic wear value (PAV) : perspex (Perspex) to which this examination contacted suspension of silica in sorbitol / glycerol mixture It is based on brushing a board with a head of a toothbrush. Usually, the presentation of a slurry is as follows and is a certain : silica. 2.5 g glycerol 10.0 g sorbitol syrup * 23.0 g* syrup contains 70% of sorbitol, and 30% of water.

[0023]Weighing of all the ingredients is carried out, and it puts into a beaker, and is made to

distribute for 2 minutes by 1500 rpm using an easy agitator. By Imperial Chemical Industries (Imperial Chemical Industries) PLC. A sheet of 110 mm x 55 mm x 3 mm of standard transparent perspex provided by a name of article of code (code) 000 is used for an examination.

[0024]Mid Essex, Hanp Tonhil, It examines by using what improved the wet paint scrub tester (Wet Paint Scrub Tester) made from research equipment Limited (Research Equipment Limited) of the Wellington load. This improvement changes a holder and enables it to use a toothbrush instead of a paint brush. In order to push a brush against a perspex board, 14 unciae (396.89g) weight is attached to a brush.

[0025]A galvanometer is proofread using a 45-degree plus peck (Plapec) light measurement head detector and a standard (50% degree of brilliancy) light reflector. Reading of a galvanometer is adjusted to a value of 50 under these conditions. Reading of the new board of perspex is performed using the same reflecting array.

[0026]It attaches to an after that holder of the new board of perspex. 2 cm^3 (sufficient quantity to carry out the lubrication of the stroke of brushing thoroughly) of distributed silica is placed on a board, and it takes down on a board of a brush head. Mechanical is switched on and it is a load brush head about a board. It exposes to 300 strokes. A board is removed from a holder and all the suspension is washed out. It is dried and the gloss value is measured again. A wear value is a difference of a value before wear, and a value after wear.

[0027]:plastic wear value calcium carbonate in which the following results will be obtained if this test method is applied to publicly known abrasive soap (15 microns)It was prepared by a method of 32 British patent 1264292. Silica xerogel (10 microns)25 alumina trihydrate [gibbsite (Gibbsite)] (15 microns) ... 16 calcium pyrophosphates (10 microns)14 dicalcium phosphate dihydrate (15 microns)7[0028]v)

Electrolytic concentration : measure sulfate in gravimetric analysis by carrying out the hot water extract of the silica, and depositing it as barium sulfate after that. Chlorine is measured by titration [method of a mower (Mohr)] by a standard silver nitrate solution which carries out the hot water extract of the silica, and uses potassium chromate as an indicator after that.

[0029]vi) Moisture loss in 105 ** : a weight loss of silica when it dries until weight became fixed in an electric furnace of 105 ** determines moisture loss.

[0030]vii) Ignition loss in 1000 ** : a weight loss of silica when it ignites until weight became fixed within a 1000 ** furnace determines ignition loss.

[0031]viii) pH : perform this measurement about suspension of 5%w/w of silica in boil deionized water (CO_2 is not included).

[0032]ix) It is 1000 ** and a sample of crystalline form:silica after calcination is calcinated at 1100 ** in an electric muffle furnace for 1 hour. A processed sample is made to cool and an existing crystal structure is identified from trace which can be obtained from an X-ray

diffractometer.

[0033]x) Mercury pouring capacity : measure mercury pouring capacity with a standard mercury injection method which uses a Micrometrics auto pore (Micrometrics Autopore)9220 mercury porosimeter (being a cm^3/g unit). Pore diameters receive mercury from a formula of Washburn (Washburn). Surface tension of 485 dynes/cm It calculates using a value of a 140-degree angle of contact.

[0034]Before measurement, degasifying of the sample is carried out to a pressure of 50 microns of mercury at a room temperature. mercury pouring capacity recorded -- the calculation pore diameters 0.05 -- or -- it happens over the range of 1.0 micron, and it turns out then that this expresses the true degree of particle Ko Uchida of silica, i.e., porosity of a stoma inside particles, from a mercury pouring curve.

[0035]Examples 1-5, and 7 were measured based on this. a place which investigated a pouring curve about 6 -- 0.05 -- or -- it became clear that pouring capacity recorded over the calculation pore-diameters range of 0.2 micron was suitable as true measured value of the degree of particle Ko Uchida.

[0036]xi) Refractive-index (RI) / transmissivity of appearance of silica : distribute a sample of silica in the sorbitol syrup (70% sorbitol) / water mixture of a certain range. Transmissivity of a dispersing element is usually measured by 589 nm after deaeration for 1 hour using a spectrophotometer. Water is used as blank. A refractive index of each dispersing element is also measured using an Abbe refractometer.

[0037]A graph of transmissivity plotted to a refractive index gives the range of a refractive index which shows transmissivity exceeding 70% which should be measured. The highest transmissivity of a sample and a refractive index of appearance of silica from which this is obtained can also be estimated from this graph.

[0038]xii) average pore-diameters (MPD): -- if this parameter uses a pillar model in relation to surface area and pore volume -- following formula: $\text{MPD (nm)} = (\text{pore volume (cm}^3/\text{g)} \times 4000) / \text{surface area (m}^2/\text{g)}$

It is alike and is calculated more to a silica formation thing.

[0039]Pore volume is the mercury pouring capacity which (x) defined.

[0040] radioactivity dentine attrition test (Radioactive Dentine Abrasion) (RDA) : xiii) this gentleman method, An American dental association (American Dental Association) [journal OBU dental research (Journal of Dental Research), 55 and (4) A valuation method of the degree of toothpaste wear currently recommended by 563 and 1976] is followed. In this method, human being's extracted gear tooth is irradiated with a neutron flux, and a standard brushing method is given. The radioactive phosphorus 32 removed from dentine in a dental root is used as an index of wear of a toothpaste examination. A reference slurry which contains

10 g of calcium pyrophosphate 10g in 0.5% solution 50cm³ of carboxymethylcellulose sodium is also measured, and RDA of this mixture is arbitrarily set to 100. Precipitated silica examined is prepared as suspension of the same concentration as phosphate, and the same brushing method is given.

[0041]xiv) Framework density by a helium pycnometer method : measure framework density (skeletal density) of a silica sample using micro metrics AKYU pick (Micrometrics Accupyc) 1330 pycnometer. A device is proofread with helium before measurement of a sample. Sufficient measurement count (usually 3 times) is performed, and it is chamber (chamber) in a device. Exact calculation of capacity and a "dead space" is enabled. Measurement of a sample is a sample first before analysis, although it is a repetition of a procedure of proofreading. It dries at 120 °C for 2 hours. Proofreading sky capacity of a pycnometer is already determined. If a sample which measured weight is put in in a chamber to each analysis, measurement will be performed automatically.

[0042]

[Example]Although the example of manufacture of precipitated silica is shown here, these are the things for explanation and are not for limiting this invention.

[0043]Example 1 - 7 heating stirring reaction vessel were used for silicate / acid reaction.

[0044]Mixing is an important element in the reaction of silicate and sulfuric acid. Therefore, the baffle plate addition heat stirring reaction vessel was designed in KEMINIYA ink (Chemineer Inc.) and Chem. Eng. 26 months and April, 1976 using the settled specification indicated to 102-110 pages. To the mixed gestalt, although the design of the turbine was alternative, it chose the device with 30 degrees of six-sheet shuttlecock pitch shuttlecock so that the mixed efficiency greatest by the minimum shearing force might be obtained certainly. When required, shearing was supplied to the reaction mixture by making it circulate through the external quantity shearing-mixing machine [Silverson (Silverson)] containing a square-socket quantity shearing screen throughout the addition to the case of Example 7 throughout the simultaneous adding of silicate and sulfuric acid of the contents of a reaction vessel of the acid I. An energy input is suitable to a required volume flow and the number of times of circulation as specified by the manufacturer.

[0045]:i) 3.2 whose solution used in this method is as follows -- or -- the specific silicate solution which has a SiO₂:Na₂O ratio of 3.4:1. ii) The sulfuric acid solution which has the specific gravity of 1.11 (16.1%w/w solution) thru/or 1.15 (21.4%w/w solution), the electrolytic solution which iii) each example defined.

[0046]The following procedures were adopted in manufacture of the precipitated silica of this invention. The concentration of reagin, the value of volume, and reaction temperature are shown in the 1st table.

[0047](A) The water of the liter was put into the container with the electrolytic solution of the

(B) liter, and the specific silicate solution of the (C) liter. This mixture was stirred and it heated to (E) **.

[0048]About the procedure (Examples 1-6 are included) added simultaneously, while stirring a specific silicate solution ((D) liter) and a sulfuric acid solution ((F) liter), maintaining temperature to (E) ** (while adding shearing if required) -- abbreviation -- (-- it added simultaneously over the period for G). It is made Kinichi Manaka of addition of the flow of a silicate solution and an acid solution, and the fixed pH value was certainly maintained by abbreviation 8.5 thru/or about 10.5 within the limits in the container.

[0049]sulfuric acid of sufficient quantity to make all the silicate exist from the time of the start of a reaction, and give pH 10.5 in the case of Example 7, -- (-- it added over the period for G).

[0050]In the case of Example 6, the slurry was ripened between the (H) parts by (E) ** after that.

[0051]while continuing stirring in all the examples (however, Silverson shearing is not used) -- sulfuric acid solution (II) -- (-- it added over the period for K) and pH of the slurry was reduced to the range of 2.5 thru/or 5.0. Addition (II) Naka of this acid and temperature were maintained by (E) **.

[0052]In Examples 1, 4, and 5, in addition (II) in process [of this acid], and pH 5, temperature was raised to 98 ** and it went hot water aging between the (J) parts. Although addition of acid (II) following aging was started at this high temperature, heat was not applied further. In these examples, pH was lowered to the range of 2.5 thru/or 4.0, and the aging process was stopped.

[0053]The obtained slurry was filtered after that, it washed with water, and the superfluous electrolyte was removed. Typically, to the use of toothpaste, an electrolyte is less than 2% based on dry weight. Flush drying of the filter cake of each example was carried out after washing, water was quickly removed from silica so that structure might be maintained, and it pulverized to the desired size range.

[0054]The obtained precipitated silica had the characteristic of having been expressed based on the dry weight shown in the 2nd table.

[0055]In the transparent toothpaste which contains them, the amorphous silica manufactured as indicated in the example 8 Examples 1-7 showed the satisfying washing characteristic. These toothpaste had stability and the characteristic that it is commercially suitable about use. The typical presentation which uses the silica of this invention is shown below.

[0056]

Transparent gel toothpaste weight % SORUBOSHIRU (Sorbosil) TC 15 Silica 6.0
carboxymethylcellulose-sodium 0.7 sorbitol of 10.0 this invention, 70% amorphous 61.1
polyethylene-glycol 1500 5.0 sodium lauryl sulfate 1.5 mono[sodium] fluorophosphate 0.8
flavor agent 1.0 saccharin 0.2 colorant, Blue and CI42090 It is the initial density of

characteristic-to 0.015 water and minor constituent 100. g/cm³ (25 **) 1.37[0057]

SORUBOSHIRU TC 15 is the concentration (thickening) silica which can be obtained from Crosfield chemical (Crosfield Chemicals) of Britain and Wellington.

[0058]Examples 1 and 2 of example 9 European-patent 0143848 and Examples 1, 2, and 3 of European patent 0139754 were repeated. Although it was a plant batch scale by which Example 1 must be scaled down about European patent 0143848 (large surface area silica), Example 2 was preparation of the laboratory scale, and in order to acquire sufficient sample process, it doubled batch size. The variable on all the processes indicated to be important during this patent was followed. The example from small surface area silica (European patent 0139754) was repeated according to instruction of this patent.

[0059]The 3rd table shows the characteristic of the silica by repetition of the example of this quotation with the example of this invention. All the amorphous silica of the example by which conventional technology was manufactured showed a low plastic wear value (less than 10) and high oil absorption.

[0060]

[Table 1]

第 1 表

実施例番号	1	2	3	4	5	6	7
容器容積 (リットル)	64	64	64	64	64	300	64
水体積 (A) (リットル)	7.9	18.0	13.1	9.8	9.8	68.1	12.6
使用した電解質	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl
電解質の濃度 (N/w)	25	25	25	25	25	25	25
電解質の体積 (B) (リットル)	6.8	1.7	0.9	3.8	3.8	5.1	2.4
珪酸塩重量比率 SiO ₂ /Na ₂ O	3.22	3.30	3.29	3.25	3.22	3.28	3.26
珪酸ナトリウム中の SiO ₂ 濃度 (N/w)	17.39	17.49	16.52	16.77	17.39	16.61	17.41
珪酸塩体積 (C) (リットル)	0.1	0.1	0.1	0.1	0.1	0.61	10.4
珪酸塩体積 (D) (リットル)	9.5	14.2	11.4	11.2	10.7	60.3	0
酸濃度 (N/w)	18.1	18.5	18.1	18.2	17.8	17.5	18.0
酸体積 (F) (リットル)	5.1	7.6	5.7	5.9	5.7	26.3	5.4
温度 (E) (°C)	50	80	98	50	50	98	98
酸 I 添加時間 (G) (分)	20	20	40	20	20	20	20
酸 II 添加時間 (H) (分)	10	10	10	10	5	10	10
熟成時間 (I) (分)	0	0	0	0	0	10	0
熟成時間 (J) (分)	40	0	0	40	40	0	0

[0061]

[Table 2]

第 2 表

実施例番号	1	2	3	4	5	6	7
表面積 (m^2/g)	397	307	262	361	415	145	336
平均細孔直径 (nm)	2.9	6.0	6.9	3.1	3.0	8.2	9.6
プラスチック磨耗値	23	16	20	22	20	20	16
最大透過率 (%)	83	77	78	76	77	84	71
右の屈折率において	1.437	1.440	1.440	1.436	1.436	1.442	1.438
1100°Cで焼成後の形態(*)	Ac	Ac	Ac	Ac	Ac	Ac	Ac
水銀注入容積 (cm^3/g)	0.29	0.46	0.45	0.28	0.31	0.30	0.81
1000°Cでの強熱損失 (%)	7.0	10.0	7.0	6.4	7.5	9.9	8.2
105 °Cでの水分損失 (%)	0.7	5.1	2.8	1.6	2.6	3.5	3.2
pH	6.9	7.5	6.3	6.9	6.9	7.2	7.3
電解質濃度 SO_4^{2-} (%)	0.08	0.05	0.11	0.10	0.06	0.11	0.05
電解質濃度 Cl^- (%)	0.03	0.06	0.06	0.02	0.02	0.07	0.01
油吸収 ($\text{cm}^3/100\text{g}$)	80	120	110	75	80	125	110
粒度分布 (ミクロン)							
10百分位数	3.2	3.3	3.5	3.2	3.2	2.8	2.7
50百分位数	7.7	7.8	7.2	7.1	7.9	8.3	11.5
90百分位数	12.1	12.0	12.5	11.9	15.4	19.0	18.0
20ミクロンより大の粒子 (%)	<1.0	7.0	2.0	2.0	5.7	8.4	9.0
25ミクロンより大の粒子 (%)	<0.1	<2.0	<1.0	<0.1	3.7	4.4	4.6
ヘリウム密度 (g/cm^3)	2.0764	2.0346	2.0836	2.0943	2.0852	2.1493	2.0448

(*) Acはアルファキャストバルを示す。

[0062]

[Table 3]

第 3 表

実施例	BET表面積 (m^2/g)	油吸収 (cm^3/g)	見掛けの 屈折率	重量平均粒度 (μm)	プラスチック 摩耗値	1100℃で焼成 後の X 線相
欧州特許0143848 実施例 1	374	170	1.459	15.0	6	非晶質
欧州特許0143848 実施例 2	476	200	1.457	16.0	3	非晶質
欧州特許0139754 実施例 1	24	160	1.438	16.0	8	非晶質
欧州特許0139754 実施例 2	22	175	1.448	16.6	6	非晶質
欧州特許0139754 実施例 3	47	185	1.437	16.4	3	非晶質
本発明の実施例 3	262	110	1.440	7.2	20	α -クリストル石型
本発明の実施例 6	145	125	1.442	8.3	20	α -クリストル石型

[Translation done.]